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REPORT

CD NO.

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COUNTRY	USSR	DATE OF INFORMATION 1950
SUBJECT	Scientific - Chemistry, oxidation of petroleum products	
HOW PUBLISHED	Monthly periodical	DATE DIST. 23 Apr 1951
WHERE PUBLISHED	Moscow/Leningrad	NO. OF PAGES 8
DATE PUBLISHED	Sep 1950	
LANGUAGE	Russian	SUPPLEMENT TO REPORT NO.

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THIS IS UNEVALUATED INFORMATION

ON THE MECHANISM OF THE EFFECT OF COLLOIDAL
QUASI-HETEROGENEOUS CATALYSTS ON THE PROCESS
OF LIQUID-PHASE OXIDATION OF KEROSENE FRACTIONS

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Submitted 12 Sep 1949

/The authors point out that the liquid-phase process of oxidation of kerosene fractions has been mastered by USSR industry.

The significance of the work reported on by Tsyskovskiy and Kiseleva may be illustrated by the following information, taken from an article by Candidate of Technical Sciences D. S. Velikovskiy "Specific Properties of Oxidized Petroleum Products and Their Utilization for the Solution of Actual Problems in Petroleum Refining and Conversion," published in Trudy Moskovskogo Neftyanogo Instituta imeni I. M. Gubkina, No 5 (Jubilee Issue, 1920-1945), Gostoptekhizdat, Moscow/Leningrad, 1947, pp 251-356./

As distinguished from work done in Germany, the purpose of industrial oxidation of long-chain hydrocarbons in the USSR and of research carried out in connection with that industrial process is not production of straight-chain fatty acids resembling as closely as possible the natural acids of fats and therefore capable of replacing the latter. The absence, until recently, of a supply of synthetic paraffin in the USSR together with the relative shortage of petroleum paraffins in that country have made a development of this type impossible. Oxidation of petroleum hydrocarbons therefore is carried out primarily with the aim of producing substances which may be chemically different from natural fatty acids (they necessarily are because of the high content of naphthenes in the crude material), but still are useful in the manufacture of surface active compounds and for other purposes by virtue of possessing specific properties which are different from those of natural products.

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Among the uses developed for such products may be cited the breaking of petroleum emulsions, production of cutting emulsions for metalworking, manufacture of lubricating greases, and utilization of the structure-destroying properties of such products as a means of increasing the yield of oil in the dewaxing of crude oils either in the presence of polar or nonpolar solvents. Still other applications have been envisaged.

Work on the problems in question is being conducted on a cooperative basis by the Moscow Petroleum Institute imeni Academician I. M. Gubkin, TsIATIM (Central Institute of Aviation Fuels and Oils), and the Leningrad Laboratory of Glavneftesnab (Main Administration of Petroleum Supplies). It was started in 1939 and, after an interruption caused by World War II, has continued up to the present.

/The paper by Tsyakovskiy and Kiseleva follows. Figures and tables referred to are appended./

One of the most complex questions arising from the investigation of the oxidation of petroleum hydrocarbons is undoubtedly that of catalysts. At the same time, catalysis is a powerful means which, after having been completely investigated, will allow in the near future the transformation of the oxidation method into one of the fundamental, leading processes in the chemical treatment of petroleum.

Notwithstanding the fact that contemporary ideas on the mechanism of the reaction of oxidation of hydrocarbons have been formed under the influence of research of many years, the total of the accumulated knowledge has turned out to be inadequate, so that up to now there is no unified, universal, and exhaustive theory of oxidation which could get general recognition.

The question of the mechanism of oxidation and the applicability of this or that theory to this question, as Chernozhukov pointed out correctly [1], becomes complicated, especially in the case of complex mixtures of hydrocarbons as distinguished from individual hydrocarbons. Even greater difficulties are encountered in the study of the oxidation of complex mixtures of hydrocarbons in the presence of various catalysts.

For the creation of prerequisites for formulating a uniform conception of the oxidation of hydrocarbons of this type, we thought it expedient and essential first of all to study in detail one of the fundamental links, namely, the mechanism of the action of catalysts in liquid-phase oxidation, especially on the kerosene fractions.

The choice of this direction of the investigation was dictated by the fact that the liquid-phase process of oxidation of kerosene fractions has, at this time, been mastered by industry, so that the greatest amount of experience has been gathered along this line.

In the material published below, we point out a number of phenomena which were observed in the process of oxidation of various fractions of kerosene in the presence of colloidal quasi-heterogeneous catalysts.

The first stage of any oxidation process, as treated in contemporary literature sources, is characterized by the name of "induction period." It is definite that this induction period cannot be a phenomenon of any constancy but depends on the physicochemical condition of the raw material, the quantity and quality of the catalyst, the temperature, etc.

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The literature does not give an exact characterization of this stage, but it is generally assumed that the induction period is the time in the course of which the oxidation process is greatly slowed down and in which no noticeable accumulation of reaction products is observed.

The question of the role and the behavior of the catalyst during this period cannot be answered in detail on the basis of the available investigations. It is known only that the presence of positive oxidation accelerators shortens the induction period.

Despite the above adduction of information characterizing the induction period, and clarifying the phenomena which accompany it together with its role in the entire process of oxidation, nearly everything is still in a state of flux. Our observations showed that the induction period is one of the most important and one of the main stages of the oxidation reaction. During this period, the catalyst performs its own fundamental functions, and the conditions giving the oxidation reaction the corresponding velocity and direction are created.

Experimental Part

As the object for our study we used a catalyst of the acidic manganese naphthenate type, prepared from fractions of naphthenic acids (obtained from fractionation of refined pure naphthenic acids under a residual pressure of 4 mm Hg) with an acid number of 231.3 mg KOH per gram.

The naphthenic acid fraction used for the preparation of the catalyst did not contain hydrocarbon components or any inorganic salts.

The manganese naphthenate was prepared by the double decomposition of sodium salts of naphthenic acids (in the presence of the kerosene selected for the experiment) and chemically pure manganese sulfate, used in an equimolecular quantity.

The refined solution of manganese naphthenate in the kerosene, obtained by this method, did not contain any cations of other metals, or sulfate or other anions.

The kerosene fraction used in the experiment covered a wide boiling point range, evaporating within the limits of 180 to 310°C, and containing the following groups of compounds by percent: alkanes 49.70, cyclanes 31.83, aromatic hydrocarbons 18.38.

The observation of the processes taking place during the liquid-phase oxidation was carried out in an apparatus specially constructed for this purpose (See Figure 1). The apparatus (reaction vessel) was designed in such a way that it easily permitted the measuring of photocalorimetric characteristics of the solution being examined throughout the process. The method of operations was as follows: A strictly constant gravimetric quantity of kerosene fraction (250 g) was introduced into the reaction vessel. The kerosene was heated inside the vessel to the required temperature and with a constant rate of the bubbling of air.

When the medium had reached the required temperature, the catalyst solution, which was heated to the same temperature in all experiments, was introduced. At the moment when the entire quantity of catalyst had been introduced, the conditions were corrected and the observation of the process was carried out. The temperature during the experiment was maintained with an accuracy of ±1°.

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At the moment of the introduction into the substrate of the catalyst, the photocurrent (i_o), which remained constant throughout the experiment, was fixed at a known value. The values for the photocurrent (i_1) throughout the experiment for each period of time served to characterize the phenomenon of color change of the solution, a phenomenon which indicates the advance, of the oxidation process.

Discussion of Results

The control experiments showed that from the moment of the introduction of the catalyst into the substrate, an uninterrupted increase in the intensity of the coloration of the solution was observed, and that this coloration, after having reached a maximum, decreased again.

The indicated phenomenon, which turned out to be regular, was registered in many cases, and therefore formed the basis of the planned experiment.

The change of coloration of the solution appeared, seemingly, as the consequence of some change taking place in the state of the catalyst.

We measured the relative increase of the light absorption of a kerosene solution (log i_o/i_1) with various concentrations of catalyst, with the other conditions equal, and obtained thereby a series of very characteristic curves (see Figure 2). In all cases it was found that the increase in the light absorption, which grows slowly at the beginning of the experiment, after a definite interval of time, rises sharply. This holds true for every given concentration of catalyst. According to this, the value of log i_o/i_1 rises up to a certain limiting value. Further on, the solution becomes lighter, and the value of log i_o/i_1 goes down steadily.

Samples of the solution examined under the microscope showed no change in the solution up to the value of log i_o/i_1 max. However, as soon as this value goes up to the limit, a large quantity of crystals appears in the field of vision of the microscope. This bears out the fact that the catalyst changes from the colloidally soluble state to another state, in this case suspended particles of a dimension of 3 to 5 μ.

From the moment of the decrease of the value of log i_o/i_1, a clear and uninterrupted increase in the size of the particles was observed. This period was marked and could be observed visually due to the sudden lightening of the solution.

It was thus established that the catalyst in its colloidally soluble state is found in the substratum for a very short period and then goes over into a new state. We shall conditionally call this period the primary state of the catalyst. This assumption is possible because during the time of the increase of the value of lg i_o/i_1 no visible changes take place in the state of the catalyst.

It has been established that with increase in the concentration of active catalyst -- in other words, concentration of active metal -- introduced into the substrate, the phenomenon of the transformation of the catalyst into the new state is repeated, but the character and the time during which it is registered are different.

The higher the concentration of active catalyst, with the other conditions of the experiment unchanged, the more rapidly its transformation into the new state will set in, or, in other words, the shorter will be the duration of the primary state.

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If the experiment is continued even further so that the catalyst will go over into the new state, we discover a constant increase in the mass of the particles of the catalyst with a reduction of their number in the substrate.

The increase in the mass of the particles of the catalyst changing its state contributes to the fact that its particles tend to leave the substrate and settle on the wall of the reaction vessel under the influence of the force of gravity.

After a definite time interval (depending on the concentration of the active metal, the temperature, etc.), no noticeable traces of catalyst remain in the substrate. This is clearly confirmed by the steady decrease in the ash content of the kerosene fraction being oxidized, which, after a while, has the same ash content as fresh kerosene (without catalyst) used for the test (see Table 1). From this statement it is seen that the catalyst does not remain in the substrate during the entire oxidation process. The higher the temperature of the experiment, the quicker the catalyst is removed. With the increase in temperature, the duration of the primary state of the catalyst is sharply reduced (see Table 2), and the influence of the concentration of the catalyst is less pronounced.

One of these important factors, such as the velocity of the air (its consumption for the given apparatus), although capable of modifying not only the rate, but also the direction of the oxidation reaction, in this case does not modify the duration of the existence of the primary state of the catalyst (see Table 3).

Despite the sharply increasing concentration of oxygen in the air per unit of time, the duration of the primary state of the catalyst remains unchanged for every given concentration /of the catalyst/. This permits us to assume that the concentration of oxygen in the air is not the primary factor which establishes the prerequisites for the acquisition of new properties by the catalyst, and that this factor exerts a regulating effect on the direction and rate of the reaction much later.

From the beginning of the experiment, i.e., from the moment of the introduction of the catalyst into the heated substrate with a definite concentration K, the acid numbers of the solution begin to increase. The increase of the acid numbers of the solution, although very insignificant, takes place uninterruptedly and serves as evidence of interior change in its chemical composition. It can be assumed that the change of the acid numbers of the solution takes place either at the expense of the change of the chemical composition of the substrate itself, or of the organic parts of the catalyst. Most likely both explanations are valid.

The new physical forms acquired by the catalyst may arise, it seems, because of the fact that it undergoes a chemical change due to the effect of oxidation products, which are accumulated during that period, or due to a direct destruction of the anions of the catalyst by the oxygen of the air. The latter statement, however, does not agree well with the material compiled above. In fact, the increase of the air velocity, and consequently, of the concentration of the oxygen of the air, have no influence on the duration of the primary state of the catalyst. What probably takes place in the first case is an accumulation of some oxidation products and their subsequent reaction with the anions of the catalyst. The sharp increase of the acid number of the substrate is observed only after the catalyst's transformation into a new state.

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Evidently, the considerable increase of the acid number could not have taken place until the reaction between the accumulating oxidation products and the organic parts of the catalyst has been completed (see Figure 3). The future will show to what extent this assumption is correct. In any case, energetic development of the process of oxidation can take place only upon the conclusion of the period during which the catalyst is present in the primary state.

It is interesting that there is a definite correlation between the moment when the recorded peroxide compounds appear and the transition of the catalyst into the new state. The peroxides appear after a little while, after the catalyst has acquired new properties. That this is not a chance occurrence is borne out by the fact that the time of the appearance of the peroxides at various concentrations of catalyst is changed analogously to the change of the period of existence of the first state of the catalyst.

The analysis of the phenomena observed shows that the "induction period" in the catalytic process of oxidation is ended at the moment when the catalyst has acquired new physicochemical properties. Consequently, the induction period of the catalytic process of oxidation is the period of time during which far-reaching changes take place in the material of the substrate as well as in the material of the catalyst. This period appears more important, in that it undoubtedly predetermines the quantity and the quality of the final result of the oxidation reaction.

In conclusion, we would like to express our thanks to O. R. Kuznetsov who has actively participated in the practical aspects of the present work.

Conclusions

1. The induction period of the catalytic oxidation reaction is the time during which the colloidal quasi-heterogeneous catalyst assumes new physicochemical properties.

2. The transition of the catalyst into the new state is a regular phenomenon for any conditions under which the oxidation process is carried out.

3. The time of transition of the catalyst into the new state is functionally connected with its initial concentration and temperature, but does not depend on the concentration of oxygen of the air introduced into the oxidizable substrate.

4. The catalyst is not present in the sphere of the oxidation reaction until its conclusion.

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Table 1. Time Within Which the Ash Content of the Substrate Being Oxidized Becomes Equal to the Initial Ash Content of the /unreacted/ Substrate

Temp of Expt (^{o}C)	Time (min) Within Which the Ash Content of the Substrate Becomes Equal to 0.0072%
110	217.0
120	135.0
130	87.0
140	40.0
150	20.0

Table 2. Relation Between the Period of the Primary State of the Catalyst, Its Concentration, and the Temperature of the Medium

Conc of Catalyst (on basis of metal) in Weight Percent in Relation to Weight of the Substrate	Duration of Primary State of Catalyst at a Temp of					
	110°C	120°C	130°C	140°C	150°C	160°C
	Minutes					
0.04	120.0	30.8	26.8	12.0	7.0	2.5
0.08	89.5	30.0	25.0	10.0	7.0	2.5
0.12	73.16	25.5	23.7	7.5	3.5	1.5
0.16	65.0	19.3	20.0	7.5	3.5	0.5
0.2	56.0	18.6	17.0	7.5	2.5	0.5

Table 3. Relation Between the Period of the Primary State of the Catalyst and the Velocity of the Air at Constant Temperature

Conc of Catalyst (on basis of metal) in Weight Percent	Duration of Primary State of Catalyst at the Air Velocity of					
	7.2 cm/sec	9.5 cm/sec	11.9 cm/sec	14.3 cm/sec	16.7 cm/sec	19.0 cm/sec
	Minutes					
0.04	16.0	16.5	16.5	16.5	17.0	16.9
0.06	15.05	16.4	16.3	16.2	16.3	16.5
0.12	14.1	15.9	15.0	15.3	15.5	15.8

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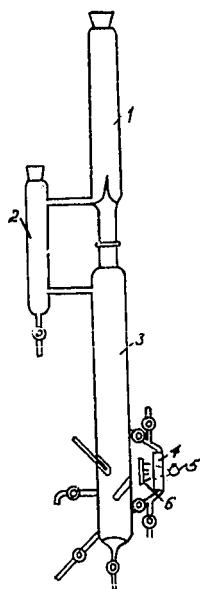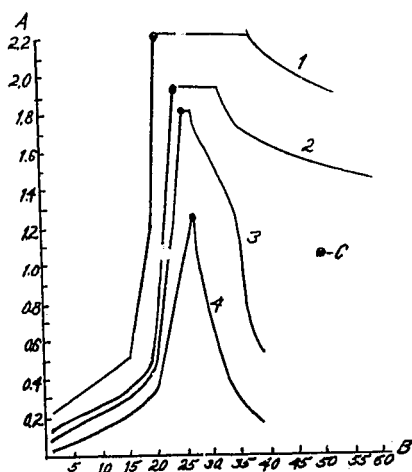

Figure 1. Apparatus for Investigating the Liquid-Phase Oxidation Process

1- Fractionating column
2- Water separator
3- Oxidation column
4- Outlet
5- Light source
6- Photoelement

Figure 2. Dependence of the Light Absorption by the Kerosene Solution on Various Concentrations of Active Catalyst at Constant Temperature

Figure 3. Dynamics of Oxidation as Function of the Concentration of Catalyst Under Constant Experimental Conditions

A- Intensity of light absorption, expressed by the logarithm of the ratio of photo currents $(\lg i_0/i_1)$
B- Time from the start of the experiment (in min)
C- Appearance of particles of changed catalyst; concentration of catalyst K (in percent relative to the substrate tested): 1 - 0.16; 2 - 0.12; 3 - 0.06; 4 - 0.04
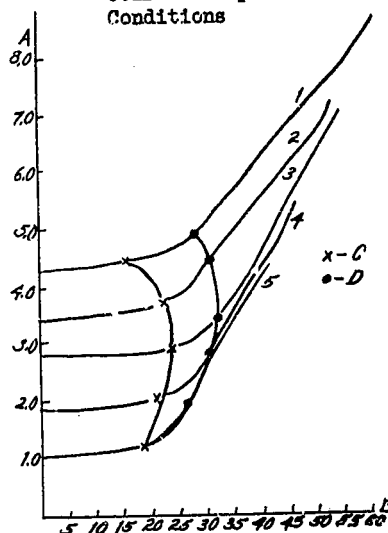
A- Acid number of the solution (in mg KOH)
B- Time (in min)
C- End of the period of the primary state of the catalyst
D- Appearance of peroxides K (in percent): 1 - 0.2; 2 - 0.16; 3 - 0.12; 4 - 0.08; 5 - 0.04

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